THE ELECTRON MICROSCOPE AS A TOOL IN CHEMICAL RESEARCH

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The electron microscope has become firmly established as a research instrument in many of the leading laboratories in this country since its introduction just a few years ago. Much research has continuously been done on the instrument itself. Most of the early research involving the instrument was, of course, of an exploratory nature in order to ascertain just what it could do. In very recent times, however, the electron microscope has assumed an important position as a research tool and has in several instances become of use in routine control work of a less fundamental nature. The two main advantages of the electron microscope over the conventional optical microscope are the large useful magnification and the great depth of focus which the new instrument makes possible.

In order for the eye to see an object, its image must subtend an angle of at least 1.4 minutes at the eye. Since the average person can not focus his eye on anything closer than ten inches, it may be derived that the smallest object which can be seen by the unaided eye is 0.1 millimeter.

It was shown some years ago by Abbe and others that a microscope, no matter how perfect it may be, can not separate two points at a distance apart of less than about one-half the wave length of the light. This means that a microscope using visible light can not resolve two points closer together than 2000 angstrom units. In view of this fact it follows that a manification of 0.1 mm. ÷ 2000 A°, or 500 times, is the maximum useful magnification of the optical microscope; this simply means that at a magnification of 500 times the maximum of detail is visible. Of course it is often convenient to use magnifications two or three times greater than that simply to ease eye-strain. Because ultra-violet light has a wave-length approximately one-half that of visible light, the closest proximity of two points for resolution in an ultra-violet microscope is about one-half that for a visible light microscope, and the corresponding maximum useful magnification is about 1000 diameters.

The depth of focus is inversely proportional to the numerical aperture of a lens. Glass optical lenses may have a numerical aperture of about one, with a corresponding depth of focus of 0.04 microns.

In order to increase the available useful magnification it was necessary to find some type of light-beam with a still shorter wave length. The development of the field of electron optics has fulfilled this need. The wave length of an electron beam was shown to be dependent upon the accelerating voltage, and to have a value of 0.05 angstrom units for a sixty kilovolt beam. Furthermore, axially symmetrical electromagnetic and electrostatic fields were both found to be satisfactory as lenses for an electron beam. Thus came the electron microscope.

The numerical aperture of an electron lens is considerably less than that of a glass optical lens. This decrease in numerical aperture is a

factor tending to decrease the resolving power, yet it increases the depth of focus. The very short wave length more than makes up for the effect of the numerical aperture on the resolving power, with the result that the electron microscope has a depth of focus of 1.5 microns and a maximum useful magnification of nearly one-hundred thousand.

The electron microscope itself is strictly analogous to a conventional compound light microscope. Each type of instrument has a light source, a condenser lens to line up the light beam on the specimen, a specimen chamber, an objective lens, a projector lens or an eye-piece, and some means for observing or recording the image. In the light microscope the lenses are of glass, the light source is of visible light and the observation is directly by eye or on a photographic plate; in the electron microscope the light source is a hot filament boiling off electrons while the lenses are either electrostatic or electromagnetic fields, and the observation is visually of the image on a fluorescent screen or may be on a photographic plate.

The magnification of an electron lens is goverened by two factors, the speed of the electrons going through and the strength of the lens field. These factors are in turn governed by the electron beam accelerating potential and the current passing through the lens coil in an electromagnetic instrument. Therefore these quantities must be kept perfectly constant; electronic regulation provides a consistancy of within 0.005 percent. In the electrostatic instrument these two factors affect the lens oppositely so that slight variations in operating potentials do not affect the lens operation. Therefore precise voltage and current regulation is not necessary in the electrostatic instrument. However, the better results have been obtained with the electromagnetic instrument; nevertheless both systems are in fairly wide use.

Because electrons are widely scattered by air, the electron microscope must be kept evacuated during operation to about 10^{-4} millimeters. A mechanical forepump and an oil diffusion pump are continuously applied to the microscope column during operation.

The usefulness of the electron microscope has been increased by further development in instrumentation within the field of electron optics. Several models of microscope have been built by manufacturers. A small instrument is available for many control purposes, using a constant magnification and not having the versatility of a more elaborate instrument. Experimental models with higher accelerating potentials have been constructed in a few commercial and university laboratories, and a scanning instrument for studying surfaces of electron opaque materials has been investigated on an experimental basis. It was a logical development to combine electron diffraction apparatus with the electron microscope, and such dual apparatus is commercially available.

One of the more promising allied developments in the field of electron optics is the electron microanalyzer. It makes possible the chemical identification of an extremely minute section of a specimen. An electron probe is directed onto the desired portion of the specimen, the electrons then losing energy in accordance with the substance which they hit. The beam, after passing through the specimen, is magnetically spread out into its constituent energy portions, which may then be recorded photographically. The resultant spectrum reveals the chemical iden-

tity of the elements which were encountered by the electron probe. It will be possible to combine this technique with the electron microscope so that the desired portion of the specimen may be selected visually.

The scientific literature of the past few years has contained many review articles of electron microscopy, and it has also contained many articles discussing specific applications of electron microscopy. A very excellent general bibliography of the subject has been prepared by C. Marton and S. Sass, J. App. Phys., *14*, 522 (1943) and ibid *15*, 575 (1944). It is the purpose of this present article to give several typical examples of the use of this new instrument within the fields of chemistry. These applications are not intended to be thoroughly discussed, yet they are intended to be thorough enough to illustrate specific examples of the use of the electron microscope. Each of the three applications described has been or will be presented in a more complete form in the literature, and all have been done at the University of Illinois under the direction of Professor G. L. Clark. In each case the electron microscope has been used to complete or substantiate other means of investigation, and is not used as an entity in itself.

CARBON BLACKS AS USED IN DRY CELL MANUFACTURE

One of the more important ingredients which goes into the manufacture of a dry cell is carbon black, which is a part of the manganese dioxide mixture forming the body of the cell. A thorough study of the requirements for such a carbon black has been made by use of the electron microscope in conjunction with x-ray diffraction techniques. (J. N. Mrgudich, R. C. Clock. Electrochemical Society, 86th General Meeting, Oct. 1944, PrePrint 86-29).

The need for such a study became apparent in the early years of this war, when the usual type of acetylene black became difficult and, in some cases, impossible to obtain. The conclusions of this study may be enumerated as follows.

1. A suitable black must have particles that are adequately conductive; this shows up in the x-ray pattern, which must show at least a partial graphitization.

2. Surface forces determining dispersibility must be, in a satisfactory black, nicely balanced between the two extremes of clumping and complete isolation of the particles; this shows up in the electron microscope picture, which should show chain-like aggregations when the specimens are prepared from tertiary butyl alcohol suspensions.

3. A suitable black should have a particle size not more than 38 millimicrons; this may be directly measured on the electron micrograph.

The results of this investigation may be visualized in this manner. The dispersibility enables a small amount of black to mechanically form throughout the MnO_2 a web-like lattice of interconnecting chains, yet these particles must be conductive themselves (graphitized), and they must be small enough so that excessive amounts of black are not required. Other factors, such as water adsorption, surface films, interactions between MnO_2 and carbon, etc., are ignored in this visualization. Yet this method is a very rapid one, and results seem valid. An obvious objection could be raised to the use of x-rays instead of direct conductivity tests to measure partial graphitization; results of conductivity tests, however, just do not correlate with the observed effectiveness of a black in a battery, while the x-ray results do.

This study has shown a very unique and effective correlation of research tools. It now guides the production of carbon blacks for dry cells, and shows the necessary requirements for an effective one. It provides further evidence for the validity of the conductive-chain theory of carbon black conductivity in the mix.

QUENCHING OIL STUDIES

(Ind. Eng. Chem., Anal Ed. *16* 740-745 (1944).) Aluminum alloy motor castings quenched in oil in a 5000 gallon tank have exhibited increased internal strain with repeated use of the quenching oil. The quenching was from a temperature of 480°C., and apparently the oil became partially oxidized by use. A study for the evaluation of the deterioration in the oil was made by Clark and Kaye at the University of Illinois. A spectrophotelometer was the basis of the study. Relative transmission values were measured for the original oil and for oils heated in the laboratory. From these data information concerning the mechanism of the changes in the oil was obtained. Metals, such as aluminum, were found to increase the initial rate of oxidation, and various antioxidant additives were evaluated. Oil samples withdrawn from the quenching tank in the foundry revealed that the laboratory tests were truly analagous to the actual processes effective in the tank. Thus a good method for the evaluation of the oils was developed using the spectrophotelometer.

The electron microscope has had much to do with this method, as it has revealed much of the actual mechanism behind the observed phenomena. Micrographs of the oil have shown that definite solid particles are produced in the oil as it becomes partially oxidized. These particles, which are as big as 0.5 micron, are probably low molecular weight polymers. Now, the spectrophotometric observations must be based upon light absorption, fluorescence and/or scattering. The presence of these particles, as proved by the electron microscope, indicates that scattering must be a major factor. This means that the relative transmission curves must actually be a measurement of the amount of particles in the oil. The presence of these particles could conceivably have a large influence on the heat conduction of the oil, which is likely a major factor in determining the residual strain left in the aluminum casting after quenching. Further tests have shown that when the particles are removed by filtration of the oil, as indicated by electron micrographs, the residual strain in the castings is less than in those quenched before filtration.

Thus the electron microscope has revealed some of the mechanism behind a spectrophotometric evaluation of quenching oils and has aided in the development of a better oil.

AGE-HARDENING OF LIGHT METALS AND ALLOYS

("Electron Micro radiographs of Light Metals and Alloys." Thesis, University of Illinois, R. B. Fischer) (1944). Among the most prominent of the light metals and alloys finding great use in present day manufacture, especially in the aircraft industry is duralumin. Duralumin is an exceedingly hard aluminum base alloy containing usually four percent copper, and lesser amounts of magnesium, manganese, iron, and silicon. Dr. Wilm discovered thirty years ago that some aluminum alloys exhibited what is now known as age-hardening properties. A block of such an alloy, when heated, quenched, and allowed to stand at ordinary

room temperatures, increased in hardness, as shown by any standard hardness testing apparatus, for a period of hours or even days from the time of quenching. Many different alloys and heat treatments were tried out soon after Wilm's first discovery, and duralumin is a specific result of these investigations. No absolute proof of the cause nor the mechanism of this change was found at that time, and many methods of research were used in an attempt to find that cause and mechanism. For twenty-five years the usually accepted theory has been that proposed by Merica.

According to this proposal, the copper and other minor constituents are largely placed into solid solution in the aluminum upon heating due to their greater solubility at high than at low temperatures; upon quenching, a supersaturated solution is produced; upon standing, particles, chiefly of $CuAl_2$, gradually precipitate from the solid solution. These precipitated particles serve as "keys" between the grains of the metal, thus making it harder than the pure metal would be. There should be an optimum particle size at which a given amount of copper, in the form of $CuAl_2$, would produce maximum hardness. This optimum particle size was calculated to be less than the upper limit of resolution of optical microscopes; so it was not alarming to find that optical metallurgical microscopes revealed no precipitated $CuAl_2$, except in cases of relatively soft aluminum-copper alloys in which the precipitated particles were much larger than the optimum particle size referred to above.

Much work has been done on this problem of age hardening, and considerable data have been amassed along various lines: x-ray diffraction, hardness measurement, tensile strength, electrical conductivity, volume change, etc., all of which have indicated that the age hardening of duralumin is, to say the least, a very complicated and obscure process.

It was natural to investigate this problem further with the advent of the electron microscope in an effort to detect some actual microscopic evidence of the processes occurring during the hardening or aging period. Usual methods of metallographic study involving the use of plastic replicas of the metal surface, have not proved to be feasible in this particular study, so a new technique was developed, in which very thin specimens of the alloy were prepared and subjected to the entire heat treatment and aging procedure. Interpretation of the results is difficult, although some definite appearance of a precipitation during aging has been established. Thus the electron microscope has at last provided some direct evidence that the age hardening of duralumin is a precipitation process.

These three examples of recent applications of the electron microscope have illustrated several things: The instrument is of primary usefulness when used in conjunction with other instruments and methods of research; it is of great use in practical industrial problems; it is of great use in problems of a more academic nature; it has exhibited great possibilities as a tool in chemical research.

No mention has been made of the use of the electron microscope in other fields of endeavor. Probably the biological subjects proved its greatest usefulness. The reader is referred to the literature, as summarized in the bibliographies referred to above, for applications in this and still other fields.